Electronic Supplementary Information

A Ni_3N-Co_3N hybrid nanowire array electrode for high-performance nonenzymatic glucose detection

Xinglu Dai, [a] Wenqing Deng, [a] Chao You,[a] Zhen Shen,[a] Xiaoli Xiong,[a,*] and Xuping Sun[b,*]

[a] College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, China. E-mail: xiongxiaoli2000@163.com

[b] College of Chemistry, Sichuan University, Chengdu 610064, China.

E-mail: sunxp_scu@hotmail.com

Experimental section

Materials: Lactose, urea, fructose, and glucose were purchased from Beijing Chemical Works. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), sodium hydroxide (NaOH), sodium chloride, ascorbic acid, uric acid and dopamine were purchased from Aladdin Ltd. (Shanghai, China). All reagents were used as received without further purification. Titanium plate (Ti) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business and was cleaned by sonication sequentially in acetone, water and ethanol several times to remove the surface impurities. Ultrapure water was utilized to prepare all solutions.

Preparation of Ni-Co hydroxide and Ni_3N-Co_3N NW/Ti: Ni-Co hydroxide was synthesized according to the previous report.[1] 2 mM $Ni(NO_3)_2.6H_2O$), 4 mM

$Co(NO_3)_2.6H_2O$, and 15 mM urea were dissolved into 70 mL deionized water. Then the above solution and a piece of cleaned Ti plate (3 cm × 2 cm) was transferred to a 40 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h. After the autoclave cooled down naturally, the resulting Ni-Co hydroxide was taken out and washed with ultrapure water and dried at 60 °C. To make Ni_3N-Co_3N NW/Ti, Ni-Co hydroxide was placed in the furnace and heated to 400 °C with a heating speed of 5 °C min^{-1} under a flowing NH_3 atmosphere. After reacting 3 h at 400 °C, the system was allowed to cool down to room temperature naturally still under a flowing NH_3 atmosphere. Finally, the black Ni_3N-Co_3N NW/Ti was collected for further characterization. The loading for Ni_3N-Co_3N on Ti plate was 1.6 mg cm^{-2}.

Characterizations: Powder X-ray diffraction data were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) measurements were carried out on a HITACHI S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a conventional three electrode system, using Ni_3N-Co_3N NW/Ti as working electrode, platinum wire as counter electrode and Hg/HgO as reference electrode. All tests were

carried out at room temperature. All the potentials reported in this work were *vs*. Hg/HgO, and the equivalent relative to reversible hydrogen electrode (RHE) according to E (RHE) = E (Hg/HgO) + 0.866.

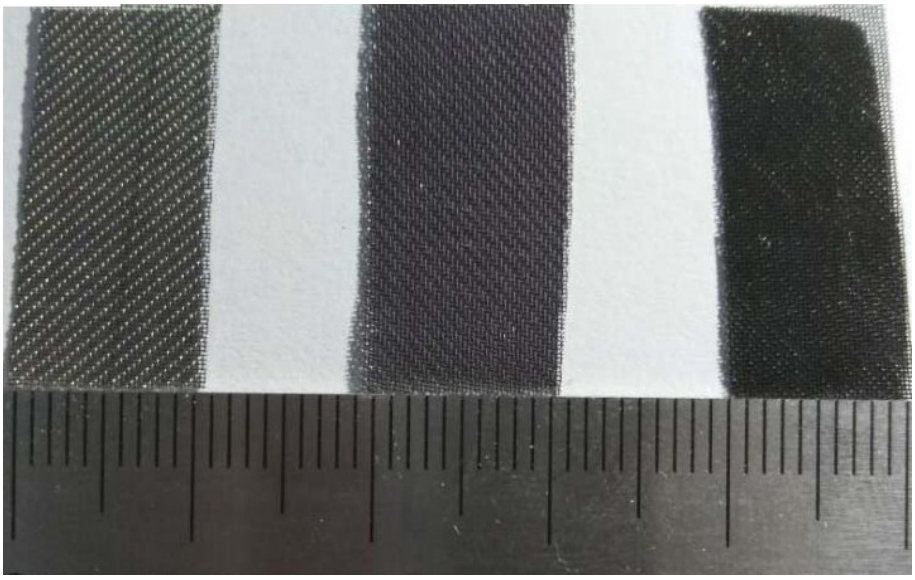

Fig. S1. Optical photograph (from left to right) of gray Ti, clay bank Ni-Co hydroxide, and black Ni_3N-Co_3N NW/Ti.

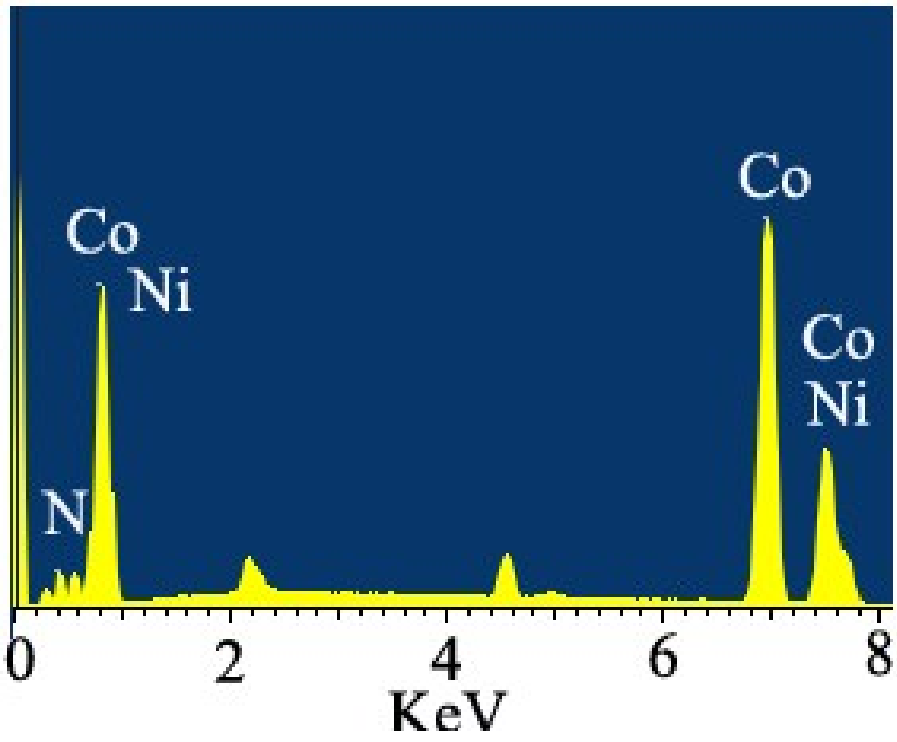

Fig. S2. EDX spectrum of Ni_3N-Co_3N NW/Ti.

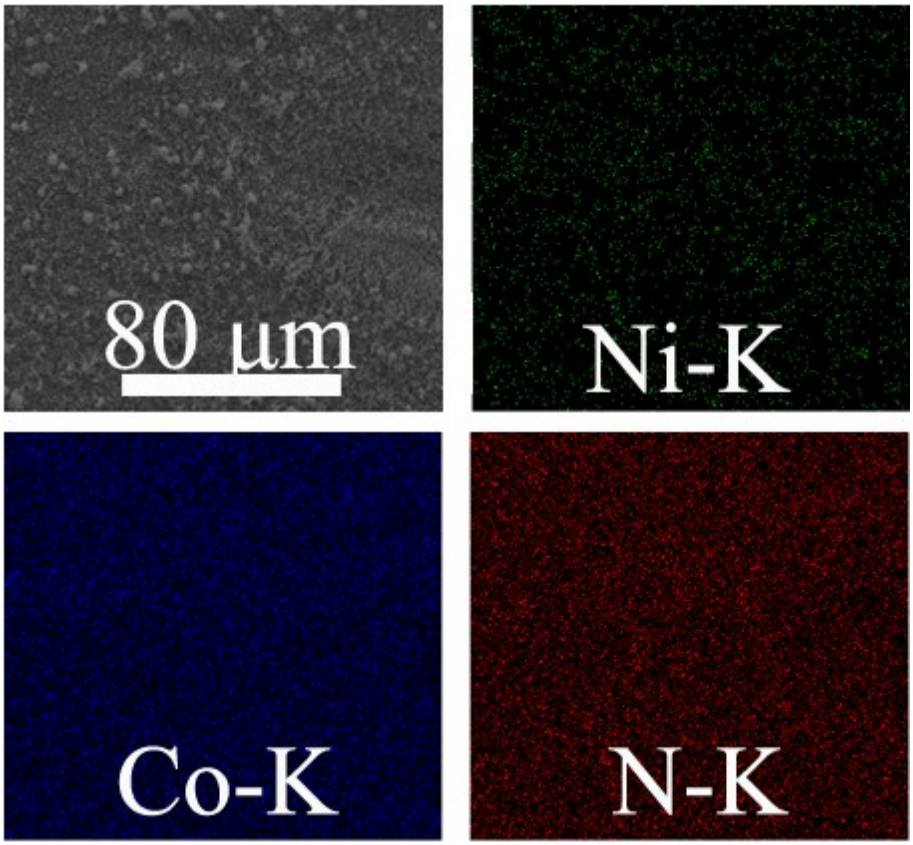

Fig. S3. SEM and corresponding EDX element mapping images of Ni, Co, and N for Ni_3N-Co_3N NW/Ti.

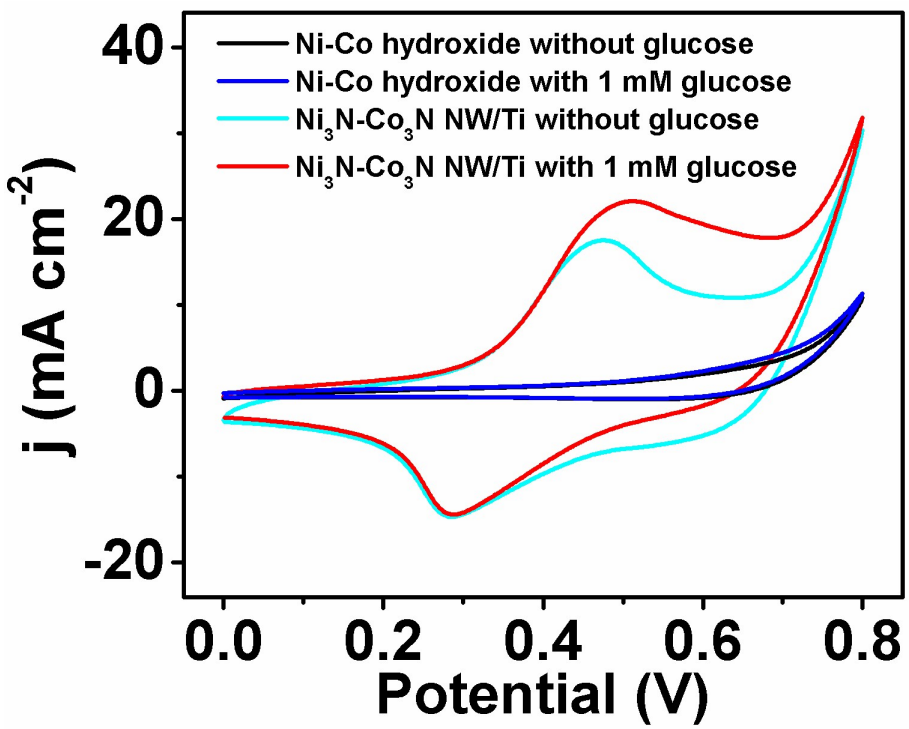

Fig. S4. CVs of Ni_3N-Co_3N NW/Ti and Ni-Co hydroxide with and without of 1 mM glucose.

Table S1. Comparison of analytical performances of Ni_3N-Co_3N NW/Ti with other Ni based and Co based non-enzymatic electrochemical glucose sensors.

Catalysts	Sensitivity (μA mA^{-1} cm^{-2})	Linear range (mM)	Detection limit (μM)	Ref.
Ni_3N-Co_3N NW/Ti	4418.7	0.0001-4.0	0.03	This work
Ni-Co-S/TM	3291.5	0.001-3.0	0.12	2
NiCoP NA/CC	14586		0.13	3
$NiCoO_2$@CNT	1424.41	0.01-1.55	1.14	4
$NiCo_2O_4$ HR	1685.1	0.0003-1	0.16	5
Co_3O_4 NFs	1440	0.005-12	0.08	6
Co_3O_4-HND	708.4	0.002-6.06	0.58	7
Co_3O_4/PbO_2 NR	460.3	0.005-1.2	0.31	8
Co_3O_4 NFs	36.25	up to 2.04	0.97	9
CNFS/$Co(OH)_2$	68000	0.01-0.12	5	10
NiO-HMS/GCE	2390	0.00167-6.87	0.53	11
Hierarchical NiO/NF	395	0.018-1.2	6.15	12
$Ni(OH)_2$/C NC	1004.6	0.001-15	0.14	13
$Ni(OH)_2$/3DGF	2650	0.001-1.17	0.34	14
$Ni(OH)_2$/Ni	1130	0.002-004	1	15
RGO-$Ni(OH)_2$/GCE	11.43	0.002-3.1	0.6	16
$Ni(OH)_2$ NF	8500	0.01-0.8	1.2	17
$Ni(OH)_2$/CILE	202	0.05-23	6	18
Ni NF	2370	0.01-0.7	5	19
Ni CFP	420.4	0.002-2.5	1	20

Table S2. Determination of glucose in human blood serum sample.

Human serum	Commercial method (mM)	Current method (mM)	RSD (%)(n=3)
Sample1	10	9.7	3.79
Sample2	4.7	4.8	2.56
Sample3	5.8	6.0	3.92

*All the concentration tests and RSD calculations are of three independent measurements.

References

1 D. Liu, Q. Lu, Y. Luo, X. Sun and A. M. Asiric, *Nanoscale*, 2015, **7**, 15122.

2 X. Cao, K. Wang, G. Du, A. M. Asiri, Y. Ma, Q. Lu and X. Sun, *J. Mater. Chem. B*, 2016, **4**, 7540.

3 Z. Wang, X. Cao, D. Liu, S. Hao, G. Du, A.M. Asiric and X. Sun, *Chem. Commun.,* 2016, **52**, 14438.

4 S. Radhakrishnan and S. J. Kim, *RSC Adv.*, 2015, **5**, 44346.

5 J. Yang, M. Cho and Y. Lee, *Biosens. Bioelectron.*, 2016,**75**, 15.

6 C. Guo, X. Zhang, H. Huo, C. Xu and X. Han, *Analyst*, 2013, **138**, 6727.

7 E. Zhang, Y. Xie, S. Ci, J. Jia and Z. Wen, *Biosens. Bioelectron.*, 2016, **81**, 46.

8 T. Chen, X. Li, C. Qiu, W. Zhu, H. Ma, S. Chen and O. Meng, *Biosens. Bioelectron.*, 2014, **53**, 200.

9 Y. Ding, Y. Wang, L. Su, M. Bellagamba, H. Zhang and Y. Lei, *Biosens. Bioelectron.*, 2010, **26**, 542.

10 Q. Wang, Y. Ma, X. Jiang, N. Yang, Y. Coffinier, H. Belkhalfa, N. Dokhane, M. Li, R. Boukherroub and S. Szunerits, *Electroanal.*, 2016, **28**, 119.

11 S. Ci, T. Huang, Z. Wen, S. Cui, S. Mao, D. A. Steeber and J. Chen, *Biosens. Bioelectron.*, 2014, **54**, 251.

12 L. Wang, Y. Xie, C. Wei, X. Lu, X. Li and Y. Song, *Electrochim. Acta.*, 2015, **174**, 846.

13 L. Wang, Y. Tang, L. Wang, H. Zhu, X. Meng, Y. Chen, Y. Sun, X. Yang and P. Wan, *J. Solid State Electrochem.*, 2015, **19**, 851.

14 B. Zhan, C. Liu, H. Chen, H. Shi, L. Wang, P. Chen, W. Huang and X. Dong, *Nanoscale*, 2014, **6**, 7424.

15 Y. Zhao, G. Gu, S. You, R. Ji, H. Suo, C. Zhao and F. Liu, *RSC Adv.*, 2015, **5**, 53665.

16 Y. Zhang, F. Xu, Y. Sun, Y. Shi, Z. Wen and Z. Li, *J. Mater. Chem.*, 2011, **21**, 16949.

17 P. Kannan, T. Maiyalagan, E. Marsili, S. Ghosh, J. Niedziolka-Jönsson and M. Jönsson-Niedziolka, *Nanoscale*, 2016, **8**, 843.

18 A. Safavi, N. Maleki and E. Farjami, *Biosens. Bioelectron.*, 2009, **24**, 1655.

19 K. O. Iwu, A. Lombardo, R. Sanz and S. Scire and S. Mirabella, *Sens. Actuators, B*, 2016, **224**, 764.

20 Y. Liu, H. Teng, H. Hou and T. You, *Biosens. Bioelectron.*, 2009, **24**, 3329.